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Plasticizers from Lactic Acid

n-ALKYL CARBONATES OF VARIOUS ESTERS OF LACTIC ACID

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Thirty-five plasticizers made by acylating esters of lactic acid with *n*-alkyl chloroformates are described. Boiling points of the plasticizers and compatibilities with cellulose acetate and polyvinyl chloride (95% vinyl chloride copolymer) were determined. Also reported are the tensile strength, modulus at 100% elongation, ultimate elongation, and brittle point of each plasticized vinyl composition. As indicated by modulus and brittle point, many of the esters are more efficient than di-2-ethylhexyl phthalate as plasticizers for the vinyl resin.

INCREASING demand for plasticizers has led to considerable work in the authors' laboratory on the preparation and evaluation of high boiling lactic acid derivatives as plasticizers. Because lactic acid is a hydroxy acid, its simple esters can be acylated with mono- or polybasic acids to make diesters of relatively high molecular weight. The presence of at least two ester groups in these compounds makes them compatible with many synthetic resins.

Earlier papers reported the use as plasticizers of diethylene glycol biscarbonates (*10*), succinates (*11*), adipates (*8, 9, 11*), sebacates (*9, 11*), maleates (*9*), phthalates (*9, 11*) and laurates (*1*) of various lactates, as well as some esters of polyacetic acid (*2*). The present paper presents data on 35 *n*-alkyl carbonates of lactates made by the reaction of alkyl chloroformates with the lactates. The preparation, physical properties, and analyses of these compounds have been reported elsewhere (*5–7*).

Table I shows boiling points of the esters and their compatibility with cellulose acetate as well as some properties of the plasticized vinyl chloride resin. When R′ was an alkyl group and R and R′ together contained a total of about 13 carbon atoms, the plasticizers had boiling points above that of dibutyl phthalate (148° C. at 1 mm.). A total of about 18 carbon atoms in R and R′ was required to produce a compound having a boiling point as high as that of di-2-ethylhexyl phthalate. Esters having a total of not more than about 10 carbon atoms in the groups R and R′ were compatible with cellulose acetate when R′ was an alkyl group. If R′ contained one or more ether linkages, the compatibility was improved so that about 13 carbon atoms in R and R′ could be tolerated.

Ether linkages in already highly oxygenated molecules caused decreased compatibility of the esters with the vinyl chloride resin, with the result that most of them bled out of the resin on aging. The decyl carbonate of decyl lactate apparently exemplifies the opposite extreme in that its incompatibility with the vinyl resin is presumably due to its preponderantly hydrocarbon nature.

The hexyl carbonate of diethylene glycol dilactate $[C_6H_{13}OCOOCH(CH_3)COOCH_2CH_2]_2O$ is unique in that it is a very

Table I. Boiling Points of n-Alkyl Carbonates of Various Lactates (ROCOOCH(CH$_3$)COOR') and Properties of the Plasticized Resins

R	R'	Formula	Mol. Wt.	Boiling Points, ° C., at Various Pressures: 0.01 mm.	0.1 mm.	1.0 mm.	10 mm.	Compatibility with Cellulose Acetate[a]	Properties of Plasticized Polyvinyl Chloride[b]: Tensile strength, lb./sq. inch	Modulus, lb./sq. inch	Elongation, %	Brittle point, ° C.	Compatibility[c]
Octyl	Methyl	$C_{13}H_{24}O_5$	260.3	53	82	117	162	C	3070	920	290	−44	C
Decyl	Methyl	$C_{15}H_{28}O_5$	288.4	73	102	138	184	I	2750	1070	280	−47	C
Amyl	Butyl	$C_{13}H_{24}O_5$	260.3	48	75	109	154	C	3180	1045	290	−41	C
Hexyl	Butyl	$C_{14}H_{26}O_5$	274.4	57	85	120	166	CI	3040	1050	340	−40	C
Octyl	Butyl	$C_{16}H_{30}O_5$	302.4	72	102	139	186	I	2910	1140	260	−48	C
Decyl	Butyl	$C_{18}H_{34}O_5$	330.5	90	120	158	207	I	2930	1130	380	−47	C
Dodecyl	Butyl	$C_{20}H_{38}O_5$	358.5	102	134	174	226	I	2920	1190	320	−59	C
Amyl	Amyl	$C_{14}H_{26}O_5$	274.4	52	81	117	165	CI	2950	1010	250	−37	C
Hexyl	Hexyl	$C_{16}H_{30}O_5$	302.4	69	99	136	184	I	2770	1020	360	−43	C
Decyl	Decyl	$C_{24}H_{46}O_5$	414.6	133	166	206	256	I	2070	1340	190	−46	I
Methyl	Decyl	$C_{15}H_{28}O_5$	288.4	70	99	135	180	CI	2960	1090	275	−48	C
Ethyl	Dodecyl	$C_{18}H_{34}O_5$	330.5	89	120	160	208	I	2940	1290	260	−45	C
Ethyl	Hexadecyl	$C_{22}H_{42}O_5$	386.6	116	150	193	246	I	3120	1460	320	−37	C
Ethyl	Cyclohexyl	$C_{12}H_{20}O_5$	244.3	44	71	105	150	C	3460	1850	220	−7	C
Butyl	Octyl	$C_{16}H_{30}O_5$	302.4	73	102	139	185	I	2980	790	340	−49	C
Butyl	Decyl	$C_{18}H_{34}O_5$	330.5	86	117	156	205	I	2750	840	260	−55	C
Butyl	Dodecyl	$C_{20}H_{38}O_5$	358.5	101	133	174	225	I	3140	1360	290	−61	C
Ethyl	Tetrahydrofurfuryl	$C_{11}H_{18}O_6$	246.3	57	85	120	164	C	3680	1860	230	−9	C
Butyl	Tetrahydrofurfuryl	$C_{13}H_{22}O_6$	274.3	70	100	136	182	C	3220	1240	280	−19	Bled
Hexyl	Tetrahydrofurfuryl	$C_{15}H_{26}O_6$	302.4	84	115	153	201	C	2970	1120	290	−23	Bled
Octyl	Tetrahydrofurfuryl	$C_{17}H_{30}O_6$	330.4	100	132	171	219	..	3480	1350	310	−30	Bled
Decyl	Tetrahydrofurfuryl	$C_{19}H_{34}O_6$	358.5	115	147	186	234	I	3140	1290	340	−37	Bled
Dodecyl	Tetrahydrofurfuryl	$C_{21}H_{38}O_6$	386.5	127	161	202	253	I	3120	1350	310	−38	Bled
Ethyl	Butoxyethyl	$C_{12}H_{22}O_6$	262.3	43	71	107	153	C	3470	1310	275	−32	C
Amyl	Butoxyethyl	$C_{15}H_{28}O_6$	304.4	69	99	136	184	C	3230	1260	300	−40	C
Decyl	Butoxyethyl	$C_{20}H_{38}O_6$	374.5	109	142	183	236	I	2985	1260	300	−55	CI / Bled
Ethyl	Butoxyethoxyethyl	$C_{14}H_{26}O_7$	306.4	78	107	143	188	C	2960	1360	310	−42	C
Amyl	Butoxyethoxyethyl	$C_{17}H_{32}O_7$	348.3	97	128	168	217	CI	3050	990	350	−43	C
Octyl	Butoxyethoxyethyl	$C_{20}H_{38}O_7$	390.5	115	148	189	241	I	2880	1010	300	−48	Bled
Decyl	Butoxyethoxyethyl	$C_{22}H_{42}O_7$	418.6	127	161	204	258	I	3100	1100	340	−51	Bled
Dodecyl	Butoxyethoxyethyl	$C_{24}H_{46}O_7$	446.6	138	174	220	277	I	2850	1290	290	−48	CI / Bled
Hexyl	Hexyloxyethyl	$C_{18}H_{34}O_6$	346.5	94	125	164	212	I	2890	1080	310	−53	C
Hexyl	Phenoxyethyl	$C_{18}H_{26}O_6$	338.4	110	142	182	232	C	3260	1300	350	−24	Bled
Ethyl	Diethylene glycol[d]	$C_{16}H_{26}O_{11}$	394.4	128	160	200	249	C	3370	2110	220	−18	I
Hexyl	Diethylene glycol	$C_{24}H_{42}O_{11}$	506.6	167	202	244	296	C	3440	1330	350	−25	C
Control													
(Di-2-ethylhexyl phthalate)		$C_{24}H_{39}O_4$	390.5	120	153	192	240	I	3070	1500	290	−32	C

[a] Films that contained 20% plasticizer (FM-6 resin, Hercules Powder Company). C, compatible; I, incompatible; CI, borderline.
[b] Vinylite VYDR (95% vinyl chloride copolymer) that contained 35% plasticizer.
[c] If the sample was greasy when prepared, it was considered incompatible; "bled" indicates that the sample was dry when new but became greasy after several months' storage.
[d] Diethylene glycol dilactate bis(ethyl carbonate)—i.e., [$C_2H_5OCOOCH(CH_3)COOCH_2CH_2]_2O$.

high boiling ester yet is fully compatible with both cellulose acetate and polyvinyl chloride.

As plasticizers for vinyl chloride resins, the ethyl carbonate of hexadecyl lactate, the butyl carbonate of dodecyl lactate, the amyl carbonate of butoxyethoxyethyl lactate, the hexyl carbonates of diethylene glycol dilactate and hexyloxyethyl lactate, and the dodecyl carbonate of butyl lactate appear to be of most interest, as judged by their boiling points and the moduli and brittle points of the plasticized resins.

Boiling Points. The boiling points shown in Table I were read from modified Cox charts (*4*) prepared from boiling points determined with an improved tensimeter still (*3*). The lower boiling esters were first distilled through a 24-inch Vigreux column; the higher boiling ones were distilled through an alembic still to isolate relatively pure fractions. The pure fractions obtained were used for determination of physical properties and for plasticizer screening tests.

Cellulose Acetate Compatibility. The resin used was Hercules Powder Company's high-acetyl type FM-6. Twenty per cent plasticizer was used in all cases. The resin and plasticizer were dissolved in acetone (5% solution), and the solution was poured on glass plates, which were then placed in closed boxes so that the solvent would evaporate slowly (24 to 36 hours). The films were stripped from the glass, hung in an oven at 80° C. for 1 hour, and then examined. If clear and dry, they were considered compatible; if greasy, or if white spots were present, they were considered incompatible.

Evaluation in Vinyl Resin. The details of the procedures used in compounding and testing the vinyl plastic have been described (*10*). The test compositions were:

	Parts
Vinylite VYDR	63.5
Basic lead carbonate	1.0
Stearic acid	0.5
Plasticizer	35.0

Brittle points were determined with strips cut from molded sheets 0.08 inch thick. The equipment was similar to that described by Selker, Winspear, and Kemp (*12*).

Tensile strength, modulus at 100% elongation, and ultimate elongation were determined with a Scott IP-4 tester loaded at 80 pounds per minute.

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